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Influence of dehydration kinetics on T-O-T bridge breaking in zeolites with framework type STI: The case of stellerite

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Abstract

The thermally induced structural modifications of the natural zeolite stellerite [$Ca_8Al_{16}Si_{56}O_{144}{\cdot}58H_2O$, a = 13.5947(4), b = 18.1823(6), and c = 17.8335(6) Å, V = 4408.1(3) Å^3, space group *Fmmm*, framework type STI] were studied in a temperature-resolved X-ray powder diffraction experiment, using synchrotron radiation, in the temperature range RT-976 K. In the initial stage of heating (below 430 K) Stellerite Phase A (space group *Fmmm*) is stable, and the cell volume decreases only 0.6% to this temperature. Between 430 and 490 K most of the water is released, the symmetry lowers, and a phase transition to the collapsed so-called Phase B (space group *Amma*) is observed. In this phase rotation of the 4^25^4 Secondary Building Units causes cell volume contraction and deformation of the channel system. This new phase, at 530 K, shows the statistical breaking of T-O-T bridges in the four-rings and the migration of tetrahedral atoms to new "face-sharing" tetrahedra, which partially occlude both the channels parallel to [100] and to [001]. This framework deformation is interpreted as due to the strain induced by calcium atoms on the framework to achieve better coordination after the release of water. The new structure is stable up to 750 K and the total volume decrease is about 8%. The dehydration process causes a similar framework deformation and the transition to a collapsed phase characterized by the statistical breaking of T-O-T bridges in all zeolites with STI-type frameworks. However, comparing the results obtained with different thermal kinetics, it is possible to assume that the experimental conditions play a primary role in the mechanisms of dehydration and of framework bridge breaking.

Keywords: Zeolite, stellerite, dehydration, X-ray powder diffraction, synchrotron radiation, crystal structure